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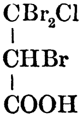
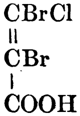
Chlortribrompropionic Acid.



$$\begin{array}{l} CBr_2Cl \\ | \\ CHBr \\ | \\ COOH \end{array}$$

β-Chlordibromacrylic Acid.



$$\begin{array}{l} CBrCl \\ \| \\ CBr \\ | \\ COOH \end{array}$$

Since the formula of β-chlordibromacrylic acid is identical with (1), the structure of the α-acid is probably represented by (2) ; or during the addition of chlorine monobromide to brompropiolic acid, the weaker halogen unites with the terminal carbon atom.

No. III. — ON β-DIBROMDICHLORPROPIONIC AND β-BROMDICHLORACRYLIC ACIDS.

By Charles F. Mabery and H. H. Nicholson.

β-Dibromdichlorpropionic Acid.

In a brief examination of the action of chlorine on β-dibromacrylic acid, it was found by F. C. Robinson and one of us,* that, although the acid was not affected at ordinary temperatures, an addition-product could readily be obtained by raising the temperature. Further study of this reaction shows that the most desirable results are obtained as regards time, as well as the quality and quantity of the product, if the temperature is kept near 100°. In one experiment after continuing the action for eight hours 5.9 grm. β-dibromacrylic acid gave 7.9 grm. of the crude β-dibromdichlorpropionic acid, which melted without purification above 90°, or ninety-six per cent of the amount of pure acid theoretically required.

The crude acid was easily purified by two or three crystallizations from a hot solution in carbonic disulphide, which deposited the greater part of the acid when cooled to 0°. It is but sparingly soluble in water, more soluble in hot than in cold chloroform, and very soluble in ether and alcohol. It crystallizes in oblique prisms, which melt at 100° and sublime slowly at higher temperatures. The composition of this acid was determined by the following analyses: —

I. 0.2142 grm. of the substance gave 0.4712 grm. AgCl + AgBr.

II. 0.8223 grm. of the substance gave 0.3485 grm. CO_2 and 0.0510 grm. H_2O.

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* These Proceedings, Vol. XVIII. p. 44.

	Calculated for $C_3H_2Cl_2Br_2O_2$.	Found.	
		I.	II.
Cl + Br	76.74	76.67	
C	11.96		11.55
H	.66		.69

The salts of this acid are comparatively unstable. We were unable to prepare a silver salt in a form suitable for analysis, since argentic bromide began to separate as soon as argentic nitrate came in contact with the acid. Although there was no perceptible decomposition of the acid when it was treated in the cold with baric carbonate, several different preparations of the salt proved on analysis to contain a quantity of barium nearly three per cent in excess of the calculated value. In the preparation of the calcium and potassium salts we found less difficulty.

Calcic β-Dibromdichlorpropionate, $Ca(C_3Cl_2Br_2O_2H) . 1\frac{1}{2} H_2O$. — On treating the acid with calcic carbonate and calcic hydrate in the cold, filtering, and concentrating by spontaneous evaporation at the ordinary temperature, the calcium salt separated in clumps of needles. After drying to a constant weight in the air the salt lost one and a half molecules of crystal water at 80°.

I. 0.7775 grm. of the air-dried salt lost 0.0307 grm. H_2O at 80°,
II. 0.9392 grm. of the anhydrous salt lost 0.0403 grm. H_2O at 80°.
III. 0.8626 grm. of the anhydrous salt gave 0.1796 grm. $CaSO_4$.

	Calculated for $Ca(C_3HCl_2Br_2O_2)_2 . 1\frac{1}{2} H_2O$.	Found.	
		I.	II.
H_2O	4.05	3.95	4.29

	Calculated for $Ca(C_3HCl_2Br_2O_2)_2$.	
Ca	6.25	6.13

Potassic β-Dibromdichlorpropionate, $K(C_3HCl_2Br_2O_2)_2 . 2 H_2O$. — The potassium salt was made by neutralizing the acid with an aqueous solution of potassic carbonate and allowing it to evaporate without the application of heat. The air-dried salt contained two molecules of crystal water, which it lost over sulphuric acid.

I. 0.8735 grm. of the air-dried salt lost 0.0809 grm. H_2O over H_2SO_4.
II. 0.7933 grm. of the anhydrous salt gave 0.2171 grm. K_2SO_4.

	Calculated for $KC_3HCl_2Br_2O_2 . 2 H_2O$.	Found.
H_2O	9.66	9.26

	Calculated for $KC_3HCl_2Br_2O_2$.	
K	11.53	12.28

β-BROMDICHLORACRYLIC ACID.

β-dibromdichlorpropionic acid is readily decomposed by alkaline hydrates, and when the reaction is allowed to progress in the cold, the elements of hydrobromic acid are eliminated with the formation of the corresponding substituted acrylic acid. The best results were obtained by treating the acid with an aqueous solution of baric hydrate in slight excess over the calculated amount, and keeping the solution slightly alkaline for twenty-four hours. Upon acidifying this solution with hydrochloric acid, dichlorbromacrylic acid was partially precipitated as an oil, which solidified when cooled to 0°. Since the acid is quite soluble in water, the solution was extracted with ether, and the total product was purified by several crystallizations from hot water.

This acid is very soluble in hot, rather sparingly soluble in cold water, and very soluble in carbonic disulphide, chloroform, ether, and alcohol. It crystallizes from water in large pearly scales, which melt at 75°–78°. Its composition was determined by analysis.

I. 0.2374 grm. of the substance gave 0.5059 grm. AgCl + AgBr.
II. 0.2034 grm. of the substance gave 0.4377 grm. AgCl + AgBr.
III. 0.7255 grm. of the substance gave 0.4433 grm. CO_2 and 0.0337 grm. H_2O.

	Calculated for $C_3HCl_2BrO_2$.	Found.		
		I.	II.	III.
2 Cl + Br	68.64	67.76	68.42	
C	16.36			16.66
H	.46			.52

In determining the solubility of this acid in cold water, a solution saturated at 20° was neutralized with baric carbonate, and the barium was determined in the filtered solution.

I. 6.0061 grm. of a solution saturated at 20° gave 0.1523 grm. $BaSO_4$.
II. 7.4519 grm. of a solution saturated at 20° gave 0.1872 grm. $BaSO_4$.

From these results the following percentages were calculated: —

I.	II.
4.79	4.74

This acid is characterized by a series of well-defined salts, several of which were prepared for analysis.

Baric β-Bromdichloracrylate, $Ba(C_3Cl_2BrO_2)_2 . 3\,H_2O$. — The barium salt was made by neutralizing the acid in aqueous solution with baric carbonate. It separated after concentration on the water-bath in prismatic crystals, which were less soluble in cold than in hot water.

I. 1.3622 grm. of the air-dried salt lost at 80° 0.1162 grm. H_2O.
II. 1.2529 grm. of the air-dried salt lost at 80° 0.1046 grm. H_2O.
III. 0.5757 grm. of the anhydrous salt gave 0.2353 grm. $BaSO_4$.

	Calculated for $Ba(C_3Cl_2BrO_2)_2 . 3 H_2O$.	Found. I.	Found. II.
H_2O	8.58	8.53	8.35

	Calculated for $Ba(C_3Cl_2BrO_2)_2$.	III.
Ba	23.82	24.03

Calcic β-Bromdichloracrylate, $Ca(C_3Cl_2BrO_2)_2 . 3 H_2O$. — The calcium salt separated in the form of rhombic plates sparingly soluble in cold water, when an aqueous solution of the acid was neutralized with calcic carbonate and concentrated on the water-bath. For analysis it was dried first at a constant weight in the air, then at 80°.

I. 1.2318 grm. of the salt gave 0.1195 grm. H_2O at 80°.
II. 1.1054 grm. of the salt gave 0.1088 grm. H_2O at 80°.
III. 0.9719 grm. of the anhydrous salt gave 0.2741 grm. $CaSO_4$.

	Calculated for $Ca(C_3Cl_2BrO_2)_2 . 3 H_2O$.	Found. I.	Found. II.
H_2O	10.15	9.71	9.85

	Calculated for $Ca(C_3Cl_2BrO_2)_2$.	III.
Ca	8.37	8.29

Potassic β-Bromdichloracrylate, $KC_3Cl_2BrO_2$. — The potassium salt was prepared by neutralization of the acid with potassic carbonate. After concentrating the solution the salt separated in minute prismatic crystals, which were very soluble in water. When dried to a constant weight in the air, it lost nothing at 80°.

1.2362 grm. of the salt dried at 80° gave 0.4144 grm. K_2SO_4.

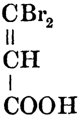
	Calculated for $KC_3Cl_2BrO_2$.	Found.
K	15.15	15.03

Argentic β-Bromdichloracrylate, $AgC_3Cl_2BrO_2$. — The silver salt was thrown down as a flocculent precipitate upon the addition of argentic nitrate to an aqueous solution of the acid. This salt is permanent in ordinary daylight, and it can be recrystallized from hot water without decomposition. It forms irregular rhombic plates, which are very slightly soluble in cold water.

0.6191 grm. of the salt dried over H_2SO_4 gave 0.2660 grm. AgCl.

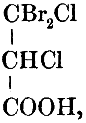
	Calculated for $AgC_3Cl_2BrO_2$.	Found.
Ag	33.03	32.34

Since β-dibromacrylic acid has been shown* to have the structure represented by the formula,



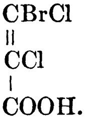
$$\begin{array}{l} CBr_2 \\ \| \\ CH \\ | \\ COOH, \end{array}$$

the chlorine addition-product would naturally have the form,



$$\begin{array}{l} CBr_2Cl \\ | \\ CHCl \\ | \\ COOH, \end{array}$$

and to the corresponding β-bromdichloracrylic acid must be assigned the formula,



$$\begin{array}{l} CBrCl \\ \| \\ CCl \\ | \\ COOH. \end{array}$$

IV. — ON ORTHOIODTOLUOLSULPHONIC ACID.

By Charles F. Mabery and George H. Palmer.

Hübner and Glassner† found that, when paraiodtoluol was dissolved in chloroform and treated with the calculated amount of sulphuric anhydride, two acids were formed, which they called α- and β-paraiodsulfitoluols. On trying the same reaction with orthoiodtoluol prepared from orthotoluidin by means of the diazo reaction, we were unable to effect any change in a chloroform solution, either in the cold or by the application of heat. But when sulphuric anhydride freshly distilled

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* H. B. Hill, these Proceedings, Vol. XVII. p. 151.

† Berichte deutschen Chem. Gesellsch., viii. 560.